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⑤④ **Glass fiber-reinforced cement press molded body and process for the production thereof.**

⑤⑦ A glass fiber-reinforced cement press molded body containing "shirasu" (amorphous fire sand-like volcanic ash) balloons in an amount of 5 to 45% by weight and, as desired, fumed silica in an amount of 5 to 40% by weight, both based on the weight of the cement, and also containing glass fibers in an amount of 1 to 7% by volume based on the volume of the molded body and a process for its production are disclosed.

**EP 0 222 339 A1**

## GLASS FIBER-REINFORCED CEMENT PRESS MOLDED BODY AND PROCESS FOR THE PRODUCTION THEREOF

### BACKGROUND OF THE INVENTION

#### Field of the Invention

This invention relates to glass fiber-reinforced cement press molded products such as rooftop heat-insulating panels, flooring, wall blocks and the like which are relatively small in size.

#### Description of the Prior Art

Hitherto, the press molded products of glass fiber-reinforced cement have been produced by mixing cement, aggregates such as siliceous sand, glass fiber and water, and press molding the mixture (see, for instance, Japanese Patent Laid-Open No. 86422/77 and Japanese Patent Publication No. 25562/78).

Conventional cement mortar was high in density because of use of siliceous sand or the like as aggregates, so that the press molded cement products were also high in density and heavy in weight. Therefore, in case of using such molded cement products for wall or ceiling, the backing or ground thereof must be strong enough to sustain the weight of such molded products. Also, these molded cement products were not easy to handle because of their heavy weight. Further, the conventional press molded cement products had the problems of possible damage to the reinforcing fibers by aggregate materials such as siliceous sand in the course of mixing operation and reduction of strength of the molding due to damage of the reinforcing fibers by said aggregates in the pressing operation. Moreover, when mixing mortar by using said conventional aggregates, many fine voids would be formed in the produced mortar due to rough particle size distribution, so that even if the mortar was molded as solid as possible, no satisfactorily close contact between reinforcing fiber and mortar could be attained, resulting in so much reduction of strength of the molded product.

### SUMMARY OF THE INVENTION

This invention has been achieved as a result of strenuous studies by the present inventors for solving said problems, and it has made it possible to obtain a glass fiber-reinforced cement press mol-

ded product which is light in weight and high in strength by mixing "shirasu" balloons as aggregates and, if necessary, further adding thereto ultra-fine particulate activated silica.

In accordance with this invention, there is provided a glass fiber-reinforced cement press molded body containing "shirasu" balloons in an amount of 5 to 45% by weight and, as desired, ultra-fine particulate activated silica in an amount of 5 to 40% by weight, both based on the weight of the cement, and also containing glass fibers in an amount of 1 to 7% by volume based on the volume of the molded body. The "shirasu" is an amorphous fine sand-like volcanic ash material.

### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In the mortar preparation according to this invention, because of use of hollow spherical lightweight and pressure-resistant aggregates such as "shirasu" balloons, which, in the course of mortar preparation, serve as a cushioning against pressure applied in the pressing step, owing to their spherical form and pressure resistance, there is no fear that the glass fibers be damaged by the aggregates, and thus the fibers are allowed to exhibit its reinforcing effect to the maximum degree. Also, said aggregates of this invention contributes to the weight reduction of the molding and makes it possible to obtain a press molded body which is light in weight and high in strength.

The "shirasu balloons" referred to in the present specification, also known as "shirasu glass micro balloons", are fine vitreous hollow bodies that can be obtained by heat treating the fine particles of glass contained in "shirasu" at a temperature of around 1,000°C for a short period of time. The "shirasu balloons" normally have an appearance of white or light brown powder, and a composition of alumino-silicate having a typical chemical analysis of 75-76% SiO<sub>2</sub>, 13-14% Al<sub>2</sub>O<sub>3</sub>, 1.3-1.4% Fe<sub>2</sub>O<sub>3</sub>, 0.05-0.12% TiO<sub>2</sub>, 0.04-0.06% MnO, 0.7-0.9% CaO, 0.12-0.20% MgO, 3.5-3.7% Na<sub>2</sub>O and 3.5-3.9% K<sub>2</sub>O, and ignition loss of 1-1.6%, but it is not limited to such compositions alone. The "shirasu" or "shirasu balloons" both are vitreous or glassy.

The "shirasu balloons" were developed by Agency of Industrial Science and Technology, Government Industrial Research Institute, Kyushu, in 1970. The "shirasu balloons" are commercially available, i.e. made and sold by Taiheiyo Kensetsu

Kabushiki Kaisha, Sanki Kogyo Kabushiki Kaisha, etc., Japan. Shirasu balloons made and sold under the trade mark of "SANKILITE" by Sanki Kogyo KK may be used in the present application. The "ultra-fine particulate activated silica" which is used optionally in this invention is the amorphous ultra-fine activated silica particles obtained by collecting and properly treating the waste gas produced in the course of production of ferrosilicon or metallic silicon in an electric furnace.

By the addition of said ultra-fine particulate activated silica (hereinafter referred to as fumed silica), the voids in the mortar, which could not be filled up when using cement and aggregates alone, can be completely filled up to enhance the reinforcing effect of fibers. Such fumed silica is also reacted with the alkaline component of cement - (pozzolan reaction) to serve as an alkalinity-reducing agent for elevating the durability of the alkali-resistant glass fibers.

Further, the fluidity of the premixed mortar is improved by the spherical form of "shirasu" balloons and ultra-small particle diameter of fumed silica, allowing the mortar to reach every corner of the mold cavity. Moreover, since a moderate degree of viscosity is afforded to the mortar, it becomes possible to prevent separation of materials at the time of pressing for dehydration.

The alkali-resistant glass fibers to be mixed in cement mortar in this invention may be any of those generally used in the art. Typically, it can be short fibers or chopped strands having a fiber length in the range of preferably 3 to 50 mm, more preferably 6 to 25 mm.

The amount of glass fibers contained in the mortar may be in the range commonly used in the art, but preferably it is in the range of 1 to 7% by volume, more preferably 2 to 5% by volume, based on the volume of the molded body. If the content of glass fibers is less than 1% by volume, no satisfactory reinforcing effect of the fibers is provided, while if said content exceeds 7% by volume, the fiber dispersion in the mortar may become non-uniform to make it impossible to obtain a homogeneous molded body.

The recommended content of shirasu balloons in the mortar is in the range of 5 to 45% by weight. If the content of shirasu balloons is less than 5% by weight, the desired weight reduction of the molding can not be achieved and also the effect of balloons for mitigating the damage to fibers proves unsatisfactory. If the balloon content exceeds 45% by weight, although the weight reduction of the molding is quite satisfactory, the bending strength of the molded body lowers to such an extent that it can hardly serve for practical use.

In this invention, fumed silica is added when it is desirable or necessary to add. In case of adding fumed silica, its content in the mortar should preferably be in the range of 5 to 40% by weight. If its content is less than 5% by weight, it can not produce its effect as an alkalinity-reducing agent for cement to a satisfactory degree. If its content exceeds 40% by weight, although its effect as an alkalinity-reducing agent is excellent, it reduces the bending strength of the molding so much as to make the molding unserviceable for practical use.

The cement used for forming the glass fiber-reinforced cement molded body according to this invention may be, for instance, Portland cement, GRC cement, moderate heat cement, blast furnace cement, fly-ash cement, alumina cement, silica cement, thermosetting cement and the like.

In this invention, it is possible to use a sheeting (netting) which has been commonly employed in the art. Use of such sheeting improves the bending strength of the molded product and reduces its deflection. For the sheeting material used in this invention, glass fibers, synthetic fibers (polyvinyl alcohol fibers, polyethylene fibers, polypropylene fibers, acrylonitrile fibers, polyamide fibers, polyethylene terephthalate fibers, etc.), and metals - (stainless steel, iron, etc.) in a form such as fibrous form are suited. The mesh size of the sheeting is preferably in the range of 5 to 40 mm, more preferably 15 to 25 mm.

The "shirasu" balloons blended in this invention play the role of a cushioning between the aggregates such as siliceous sand and the reinforcing fibers as such balloons are close to sphere in configuration, smooth in surface and hollow. Especially, they exhibit a remarkable pressure resistance in the state of being pressed at the time of press molding as they are nearly spherical in configuration, thus serving to minimize the degree of break while preventing damage to the reinforcing fibers. A material having fine open-cells such as perlite is used as light-weight aggregates in paper making, but when such material is used for press molding of glass fiber-reinforced cement, the resulting molded product proves to be high in density since said aggregate material is smashed down under pressure in the press molding operation and the cement would be forced into and fill up the fine open-cells because of the broken spherical configuration of said material and poor pressure resistance of its particles. On the other hand, in case of using "shirasu" balloons, because of their nearly spherical hollow structure and excellent pressure resistance, it is unnecessary to use a large amount of water at the time of mixing and also there is no possibility of the cement being forced into the hollow portions, thus allowing obtainment of a high-strength light-weight molded product by press

molding. When fumed silica is added to said "shirasu" balloons, there are produced such additional effects as fixing of free calcium hydroxide, further strengthening of mortar, enhancement of water tightness, reduction of cracking, etc., and further, owing to the synergistic effect of both the aggregate materials, it becomes possible to obtain a glass fiber-reinforced cement press molded body which is light in weight and high in strength, that is, high in specific strength.

#### EXAMPLES AND COMPARATIVE EXAMPLES

##### Examples 1, 2, 4-7, and Comparative Examples 2 and 3

Portland cement, siliceous sand #5, #6 and #7, "shirasu" balloons (bulk specific gravity: 0.42; particle size: not greater than 100  $\mu$ ), fumed silica - (average particle size: 0.15  $\mu$ ; silica content: 90%) and water were charged into an omnimixer in the ratios shown in Table 1, and mixed therein for one minute. Then to the mixture was further added 3% by volume of alkali-resistant glass fibers (fiber length: 13 mm, made by Nitto Boseki KK.) and mixed for 15 seconds. The thus obtained mixture was supplied into a 50 cm square plate molding device and molded under a maximum pressure of 50 kg/cm<sup>2</sup> to form a 500 mm  $\times$  500 mm  $\times$  15 mm thick glass fiber-reinforced cement plate.

##### Example 3 and Comparative Example 1

The same mixture as used in the previous examples was supplied uniformly into a hydraulic press molding device for 50 cm square plate molding so that the molding thickness would become approximately 10 mm and lightly prepressed under a pressure of 10 kg/cm<sup>2</sup>. After removing pressure, a glass fiber sheeting (mesh size: 2 cm; METSUKU - (weight per unit area): 100 g/cm<sup>2</sup>) was placed in the molding device and the mixture was further supplied into the molding device so that the total molding thickness would become 15 mm and molded under a maximum pressure of 50 kg/cm<sup>2</sup> to obtain a 500 mm  $\times$  500 mm  $\times$  15 mm thick glass fiber-reinforced cement plate.

Then the moldings obtained by the methods of Examples 1-7 and Comparative Examples 1-3 described above were cured in a moist state at room temperature for 4 weeks and their specific gravity and bending strength after curing were determined.

In order to see the strength developability per specific gravity, the specific strength (bending strength/specific gravity) was calculated.

Further, in order to know the fluidity of the material (composition), the state of filling of the composition to the corners of the molded plate was visually observed, and in order to see the durability of glass fibers, the 4-week cured moldings were immersed in water of 80°C for 3 days and their bending strength was measured.

The test results are shown collectively in Table 1.

As seen from Table 1, a glass fiber-reinforced cement molded plate having a small density but a sufficiently high strength, which is desired by this invention, can be obtained by adding the "shirasu" balloons of this invention to the cement mixture, the effect of addition of such "shirasu" balloons being clearly noted from the comparison of specific strength between Example 2 and Comparative Example 3. Also, as noted from the comparison between Examples 1, 3-5 and Comparative Example 2, a synergistic effect is produced by the addition of both fumed silica and said "shirasu" balloons, from which it is seen that, by adding said both fumed silica and "shirasu" balloons to the cement mixture, it is possible to obtain a light-weight and high-strength glass fiber-reinforced cement molded product, the product of this invention.

As described above, the cement composition containing "shirasu" balloons of this invention added thereto can minimize the damage to the reinforcing fibers by the aggregates such as siliceous sand in the course of pressing operation, and in case of further adding fumed silica to the composition, a synergistic effect of said both "shirasu" balloons and fumed silica is produced to make it possible to obtain an even more excellent glass fiber-reinforced cement press molded product.

Table 1

		Example 1	Example 2	Example 3
Composition	Portland cement (part by wt.)	100	100	100
	Siliceous sand #5 ( " )	25	25	25
	" #6 ( " )	50	50	50
	" #7 ( " )	35	50	35
	"shirasu" balloon ( " )	25	25	25
	Fumed silica ( " )	15	-	15
	Glass fiber (vol% *)	3	3	3
	Glass fiber sheeting	-	-	One layer
	Water	82	78	82
Fluidity of material		Good	Rather bad	Good
Specific gravity		1.75	1.73	1.75
Bending strength after 4-week curing (kg/cm <sup>2</sup> )		150	130	170
Specific strength (kg/cm <sup>2</sup> )		86	75	97
Bending strength after 3-day in water of 80°C (kg/cm <sup>2</sup> )		120	85	136
Bending strength retention after 3-day immersion in water of 80°C (%)		80	65	80

- to be continued -

Table 1 - (Cont'd)

Example 4	Example 5	Example 6	Example 7	Comp. Example		
				1	2	3
100	100	100	100	100	100	100
25	25	25	25	25	25	25
50	20	50	50	50	50	50
65	5	55	15	15	60	75
5	45	5	45	-	-	-
5	40	-	-	-	15	-
3	3	3	3	3	3	3
-	-	-	-	One layer	-	-
75	90	78	78	82	76	56
Good	Good	Good	Good	Rather bad	Good	Bad
1.95	1.60	1.96	1.55	1.65	2.03	2.01
142	128	137	116	104	110	130
73	80	70	75	63	69	65
99	115	82	70	62	112	78
70	90	60	60	60	80	60

Note) \* Based on the volume of the molded body.

## Claims

1. A glass fiber-reinforced cement press molded body containing "shirasu" balloons in an amount of 5 to 45% by weight based on the weight of the cement and containing glass fibers in an amount of 1 to 7% by volume based on the volume of the molded body.

2. A glass fiber-reinforced cement press molded body according to claim 1, wherein the glass fibers are alkali-resistant glass fibers.

3. A glass fiber-reinforced cement press molded body according to claim 1, wherein the glass fibers are short fibers or chopped strand.

4. A glass fiber-reinforced cement press molded body according to claim 1, wherein the length of glass fibers is 3 to 50 mm.

5. A glass-fiber reinforced cement press molded body according to claim 1, wherein the length of glass fibers is 6 to 25 mm.

6. A glass-fiber reinforced cement press molded body according to claim 1, wherein the cement is Portland cement, GRC cement, moderate heat cement, blast furnace cement, fly-ash cement, alumina cement, silica cement or thermosetting cement.

7. A glass fiber-reinforcing cement press molded body according to claim 1, containing a sheeting or netting in the molded body.

8. A glass fiber-reinforced cement press molded body according to claim 7, wherein the material of the sheeting or netting is glass fibers; synthetic fibers such as polyvinyl alcohol fibers, polyethylene fibers, polypropylene fibers, acrylonitrile fibers, polyamide fibers or polyethylene terephthalate fibers; or a metal such as stainless steel or iron.

9. A glass fiber-reinforced cement press molded body according to claim 7, wherein the mesh size of the sheeting or netting is 5 to 40 mm.

10. A glass fiber-reinforced cement press molded body according to claim 7, wherein the mesh size of the sheeting or netting is 15 to 25 mm.

11. A glass fiber-reinforced cement press molded body containing "shirasu" balloons in an amount of 5 to 45% by weight and ultra-fine particulate activated silica in an amount of 5 to 40% by weight, both based on the weight of the cement, and containing glass fibers in an amount of 1 to 7% by volume based on the volume of the molded body.

12. A glass fiber-reinforced cement press molded body according to claim 11, wherein the glass fibers are alkali-resistant glass fibers.

13. A glass fiber-reinforced cement press molded body according to claim 11, wherein the glass fibers are short fibers or chopped strand.

14. A glass fiber-reinforced cement press molded body according to claim 11, wherein the length of glass fibers is 3 to 50 mm.

15. A glass fiber-reinforced cement press molded body according to claim 11, wherein the length of glass fibers is 6 to 25 mm.

16. A glass fiber-reinforced cement press molded body according to claim 11, wherein the cement is Portland cement, GRC cement, moderate heat cement, blast furnace cement, fly-ash cement, alumina cement, silica cement or thermosetting cement.

17. A glass fiber-reinforced cement press molded body according to claim 11, wherein a sheeting or netting is contained in the molded body.

18. A glass fiber-reinforced cement press molded body according to claim 17, wherein the material of the sheeting or netting is glass fibers, synthetic fibers such as polyvinyl alcohol fibers, polyethylene fibers, polypropylene fibers, acrylonitrile fibers, polyamide fibers or polyethylene terephthalate fibers; or a metal such as stainless steel or iron.

19. A glass fiber-reinforced cement press molded body according to claim 17, wherein the mesh size of the sheeting or netting is 5 to 40 mm.

20. A glass fiber-reinforced cement press molded body according to claim 17, wherein the mesh size of the sheeting or netting is 15 to 25 mm.

21. A glass fiber-reinforced cement press molded body according to claim 11, wherein the ultra-fine particulate activated silica is fumed silica.

22. A process for producing a glass fiber-reinforced cement press molded body claimed in claim 1, which process comprises adding to cement "shirasu" balloons in an amount of 5 to 45% by weight based on the weight of the cement, mixing them with water, further adding thereto alkali-resistant glass fibers in an amount of 1 to 7% by volume based on the volume of the molded body, conducting the mixing operation, and then press molding the mixture under a pressure of 50 kg/cm<sup>2</sup> or below.

23. A process for producing a glass fiber-reinforced cement press molded body claimed in claim 11, which process comprises adding to cement "shirasu" balloons in an amount of 5 to 45% by weight and ultra-fine particulate activated silica in an amount of 5 to 40% by weight, both based on the weight of the cement, mixing them with water, further adding thereto alkali-resistant glass fibers in an amount of 1 to 7% by volume based on the volume of the molded body, conducting the mixing operation, and then press molding the mixture under a pressure of 50 kg/cm<sup>2</sup> or below.



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>4</sup> )
A	CHEMICAL ABSTRACTS, vol. 90, no. 16, 16th April 1979, page 303, column 1, abstract no. 126459h, Columbus, Ohio, US; & JP - A - 53 145 835 (KANEBO LTD.) 19-12-1978  ---	1,2	C 04 B 28/02 // (C 04 B 28/02 C 04 B 14:06 C 04 B 14:14 C 04 B 14:42 C 04 B 14:48 C 04 B 16:06 C 04 B 20:00
A	CHEMICAL ABSTRACTS, vol. 95, no. 16, 19th October 1981, page 288, column 2, abstract no. 137309p, Columbus, Ohio, US; & JP - A - 81 45860 (MATSUSHITA ELECTRIC WORKS, LTD.) 25-04-1981  ---	1,2	
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The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 19-01-1987	Examiner STROUD J.G.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			





EP 86 11 5450

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	Page 2 CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	CHEMICAL ABSTRACTS, vol. 98, no. 22, 30th May 1983, page 312, column 1, abstract no. 184622g, Columbus, Ohio, US; & JP - A - 57 191 262 (ASAHI CHEMICAL INDUSTRY CO., LTD.) 25-11-1982  -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 19-01-1987	Examiner STROUD J.G.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

(12)

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(54) **Fibre composite materials.**

(57) This invention relates to fibre reinforced cement composites and method for forming the same. The method includes the steps of mixing together dry solids and not more than 30% water by mass, based on the total dry solids contents of the mixture. The dry solids include at least one hydraulic cement, chemical pulp lignocellulosic fibre, and at least one selected siliceous substance. The mixture is formed and pressed to a predetermined density and/or dimension, with conditions of humidity thereafter being maintained for a period of time to advance setting reactions in the mixture. A fibre reinforced product is thus produced. The selected siliceous substance is defined as a natural, waste or manufactured material containing at least 50% silica and having a bulk density in discrete particle form of not more than 1200 kg per cubic metre, selected from a defined group.

## Description

This invention relates to fibre reinforced cement composites and more particularly though not solely to composites and method of manufacturing the same in the form of panels, slabs, moulded bodies and the like for such uses as components for building construction.

A set cement matrix tends to be strong in compression but weak in tension and the use of fibre reinforcement is well known in the art for the purpose of compensating in part for the deficiency in tension, thereby imparting a combination of flexural strength and fracture toughness to the product.

Various forms of hydraulic cement which set by processes including hydration are used in fibre reinforced cement composites because they have attributes of being readily available at relatively low cost, and produce a well proven matrix with acceptable strength and durability. Although ordinary Portland cement (OPC) is probably the most common hydraulic cement used for the purpose, there are many others based upon reactions between calcia, silica and alumina as the main oxides, usually in the form of a ground substantially anhydrous clinker or slag, which sets by processes including hydration when water is introduced.

Until quite recently the fibre reinforcement was almost invariably one of the natural fibrous mineral silicates, including fibrous forms of serpentine and amphibole minerals such as chrysotile, amosite, crocidolite, tremolite and actinolite, that is, the fibrous minerals commonly known collectively as asbestos.

Although asbestos has been found very effective for the purpose, it is now well recognised as being injurious to health and is seldom if ever used, except perhaps in some asbestos cement water pipes and for special applications.

Numerous fibre types have been proposed and used, as alternatives to asbestos, including various polymers and steel for example, and one of the more promising is probably carbon fibre, but its cost is prohibitive for general use at present.

Lignocellulose is also used in hydraulic cements, and in many cases gives useful results, especially when chemical pulp lignocellulosic fibre is used.

The use of lignocellulose in hydraulic cement composites can be conveniently divided into two groups: the fibre cement boards similar to asbestos cement, where chemical pulp lignocellulosic fibre is used as an alternative to asbestos, and the wood cement particle boards, where discrete wood particles are cemented together to provide panels which are usually somewhat thicker than the former type, and contain larger amounts of lignocellulose, more in the nature of a low density filler than as a reinforcement. In the latter example using discrete wood particles, the particles and cement have been found to mix together relatively easily compared with chemical pulp lignocellulosic fibre which until now has required formation of an aqueous slurry to distribute the fibres in the cement.

In the manufacture of fibre cement boards using chemical pulp lignocellulosic fibre, one of the more successful methods so far found has been to subject unbleached kraft pulp fibre to a refining or beating step which results in both fibre shortening and fibrillation, after which it may be used in what is substantially the prior art asbestos cement manufacturing technology, typically employing either the Hatschek or Magnani processes for example. The aqueous slurries from which the product is formed using these processes are difficult to de-water, due mainly to the low drainage rate caused by the fine particle size necessary for satisfactory reaction of the hydraulic cement and silica, these being the main components used.

This results in the boards being formed under quite aggressive and difficult conditions, leading to product problems of both mechanical and chemical origin when lignocellulosic fibres are used. For example, various extractives from the lignocellulose can contaminate the liquid phase of the system, and even in small amounts can seriously affect the cement setting reactions, causing rejects or a deficiency in strength. Another problem seen both in the manufacturing plant, and even once the product has been installed in a building is delamination due to poor inter-lamellar bonding, this originating from the method of sheet formation in the Hatschek process itself. These problems have been found difficult to control, resulting in rejects and loss, and higher than otherwise product costs as a consequence.

Wood cement composites are also produced by processes not unlike those used to form particle board. The wood, in the form of particles, flakes or coarse mechanical pulp fibre is mixed with cement and sufficient water for setting, and then formed and pressed into panels, often held between metal cauls until the cement has set. The discrete wood particles or pulp in this case contains both the lignin and carbohydrate components of the wood and greater amounts of extractives than chemical pulps do. Not only do these interfere with cement setting, but the high pH of the cement can cause degradation by attack of the lignin component of the wood which continues long after the cement has set. We have also seen rot in this type of product when made from Lauan peeler cores as the wood source after several years exterior exposure.

Wood cement particle board processes are of a semi-dry type which largely overcome the formation and drainage problems associated with the Hatschek or Magnani processes, but they do not enable fibre reinforced cement composites using small amounts of chemical pulp lignocellulosic fibre to be produced as the fibre is difficult if not impossible to evenly invest in the cement matrix due to problems such as clumping and balling, even when relatively short fibres are used.

Fibre cement composites have many and varied uses, and can be made from relatively inexpensive raw materials. There is therefore a need for a method of manufacturing said composites which eliminates or

minimises some of the foregoing disadvantages and problems, or which at the very least provides the public with a useful choice.

It is an object of this invention to provide method and composition for manufacturing fibre reinforced cement composites.

According to one aspect of this invention there is provided a method of forming fibre reinforced cement composites, including the steps of:

- a) preparing a mixture including dry solids and not more than 30% water by mass based upon the total dry solids content of said mixture, said dry solids including at least one hydraulic cement, chemical pulp lignocellulosic fibre and at least one selected siliceous substance;
- b) forming and pressing said mixture to predetermined density and/or dimensions; and
- c) maintaining conditions of high humidity for sufficient time to advance setting reactions in said mixture to produce a fibre reinforced product.

According to a further aspect of this invention there is provided a method of forming fibre reinforced cement composites including the steps of:

- a) preparing a mixture including dry solids and not more than 30% water by mass based upon the total mass of said dry solids, said dry solids including by mass 30% to 60% of at least one hydraulic cement, 4% to 20% chemical pulp lignocellulosic fibre, and 6% to 50% of at least one selected siliceous substance;
- b) forming and pressing said mixture to predetermined density and/or dimension, and;
- c) maintaining conditions of high humidity for sufficient time to advance setting reactions in said mixture to produce a fibre reinforced product.

According to a still further aspect of this invention there is provided a method of forming fibre reinforced composites including the steps of:

- a) preparing a mixture including dry solids and not more than 30% of water by mass based upon the total mass of said dry solids, said dry solids including at least one hydraulic cement at least one selected siliceous substance and chemical pulp lignocellulosic fibre;
- b) wherein said mixture is prepared in at least two steps, at least one of said steps including high shear and/or attrition mixing;
- c) forming said mixture to predetermined density and/or dimension, and;
- d) maintaining conditions of high humidity for sufficient time to advance setting reactions in said mixture to produce a fibre reinforced product.

According to a still further aspect of this invention there is provided a method of forming fibre reinforced cement composites including the steps of:

- a) preparing a mixture containing dry solids and not more than 30% of water by mass based upon the total mass of said dry solids, said dry solids including at least one hydraulic cement, chemical pulped lignocellulosic fibre at least one selected siliceous substance and at least one further more pozzolanic siliceous substance, being an amorphous silica or macro-amorphous silica, silica sol, silica gel, precipitated silica, biogenic silica and/or pyrogenic silica;
- b) forming and pressing said mixture to predetermined density and/or dimension, and
- c) maintaining conditions of high humidity for sufficient time to advance setting reactions in said mixture to produce a fibre reinforced product.

By definition herein throughout the specification and claims of this invention, "hydraulic cement" is a mineral binder material containing silica with calcia and/or alumina which sets or solidifies by process including hydration when water is introduced, and which includes conventional hydraulic cements, examples of which are:

- Ordinary Portland Cement (OPC) as described in British Standard No.12, 1987.
- Rapid-hardening Portland Cement as described in British Standard No.12, 1978.
- Sulphate-resisting Portland Cement as described in British Standard No.4027, 1980 (including low alkali types described therein).
- Ultra-high early strength cement, which is a more finely ground Portland Cement usually having a higher proportion of gypsum compared with Ordinary Portland Cement.
- Low-head Portland Cement as described in British Standard No.1370, 1979.
- White Portland Cement as described in British Standard No.12, 1978.
- Portland-blast furnace Cement, as described in British Standard No. 146, 1973.
- Low-heat Portland-blast furnace Cement, as described in British Standard No.4246, 1974.
- Super-sulphated Cement, as described in British Standard No.4248, 1972.
- High-alumina cement as described in British Standard No. 915,1972.
- Pozzolanic cements which satisfy the test for pozzolanicity described in British Standard 4550, 1978, (Part 2, Section 15).

Any other cement (and combinations or mixtures of the above cement examples) containing silica with calcia and/or alumina which set or solidify by processes including hydration when water is introduced.

Examples only of such hydraulic cement manufactured or available in New Zealand are those manufactured to New Zealand Standards No. 3122-1974 and/or No.3123-1974, such as Wilsons Star and Wilsons Wilsonite rapid hardening (Wilsons (NZ) Portland Cement Limited) for example, and various imported hydraulic cements such as high alumina Cement Fondu supplied by Lefarge Fondu International, and manufactured to French Standard (FNOR) P15401 and/or P15403 for example.

Any hydraulic cement or mixture of hydraulic cements containing silica, with calcia and/or alumina, which set or solidify by processes including hydration when water is introduced may be used in the present invention however.

Preferred hydraulic cements for use in the present invention are Ordinary Portland Cement, Rapid hardening Portland Cement, Portland-blast furnace Cement and Low-heat Portland-blast furnace Cement, and high-alumina cement, and mixtures of these cements.

By definition herein throughout the specification and claims defining this invention, "selected siliceous substance" is a natural waste or manufactured material containing at least 50% silica and having a bulk density in discrete particle form of not more than 1200 kg per cubic meter, selected from perlite, shirazu, pumice, volcanic tuff, diatomite, pozzolan, fly ash floaters, cenospheres, pyrogenic silica, silica fume, silica sol, silica gel, precipitated silica, biogenic silica and mixtures thereof.

Preferred selected siliceous substance for use in the present invention is perlite, shirazu, pumice, volcanic tuff, diatomite or pozzolan and mixtures of these substances, which preferably but not essentially are calcined prior to use by heat treating to a temperature of at least 450°C.

Throughout the specification and claims of this invention reference is made to the need to maintain conditions of high humidity for sufficient time to advance setting reactions in the mixture following a forming step, it being appreciated that by definition herein "hydraulic cement" sets or solidifies by processes including hydration when water is introduced. It will also be appreciated that the mixtures used in the present invention are characterised in several ways, one of which is that they contain not more than 30% water by mass based upon the total mass of the dry solids (which include hydraulic cement) of the mixture.

Since the water content of the mixture is relatively low, and is needed to effect an adequate set or solidification of the hydraulic cement we have found it essential that conditions of high humidity be maintained to prevent or at least minimise loss of the water by drying during the time required for hydration of the hydraulic cement. In the context of the specification and claims of this invention therefore, to maintain conditions of high humidity means to prevent loss of water from the formed mixture due to drying. Conditions of high humidity may be maintained in any convenient way such as containing the formal mixture within a compartment or vessel, or by covering with a flexible impermeable membrane such as a plastic cover for example. In this way the environment adjacent to the formed mixture is maintained at a high humidity and drying is prevented or minimised while hydration of the hydraulic cement advances. Once the mixture is formed, additional water may also be applied, such as by water spray or saturated steam for example. To assist in maintaining conditions of high humidity for sufficient time to advance setting reactions of hydraulic cement present in the mixture.

In the prior art, a common method for the manufacture of non-asbestos sheet has been to form from an aqueous slurry a mixture comprising Ordinary Portland Cement, ground silica and lignocellulosic fibre as the main components, and wherein the fibres are subjected to refining or beating prior to incorporating them into the mix. De-watering is a problem due to low drainage rates of the mixture, and it is usual to build up the product to the required thickness by winding a plurality of layers onto a drum prior to cutting and releasing the sheet.

The method leads to several problems including interference of the cement setting reactions due to contamination of the aqueous phase with extractives, and often poor inter-lamellar bonding between the plurality of layers. After forming, the product is subjected to autoclaving to cause a reaction to occur between the cement and the silica to product the binder matrix. The production plant is extensive, and the autoclaving step is a significant cost of production.

While some water is necessary to hydrate the hydraulic cement, we may look upon the aqueous phase of the slurry as providing a facility for mixing and transporting the components of the composite product.

In attempts to mix these components dry, or with sufficient water only to satisfy hydration of the cement, we have found (as others also have) that it is virtually impossible to invest the fibre evenly in the mixture.

Typically in the prior art the composite contains approximately 6% to 8% by weight of lignocellulosic fibre such as kraft fibre, the remainder being cement and ground silica. The high density of the cement silica mixture compared with the lignocellulosic fibre results in the volumetric ratio of these components being nearer 1:1 even though the fibre component may be only 6% to 8% by weight, and mixing in this high volume of fibre to provide an evenly dispersed mixture is a virtual impossibility. In practice, due to the need to "fluff" the lignocellulosic fibre prior to mixing, the volumetric ratio has been found to be even more adverse than the relative densities of the components would indicate. Our experiments have confirmed the results of most workers, that between 6% and 8% by weight of fibres provides a good combination of flexural strength and fracture toughness to the product, but the furnish of fibres, cement and ground silica has not been prepared from a dry mixture, but with an excess of water followed by a de-watering step.

In the manufacture of fibre reinforced cement composites in accordance with the present invention the essential fibre reinforcement is chemical pulp lignocellulosic fibre which has the advantages of ready availability, cost effectiveness, and durability, these advantages being important to the invention. Chemical pulp lignocellulosic fibre as used in the present invention may be derived from delignification processes employing alkaline and/or sulphite delignifying agents, including the soda, kraft and sulphite processes, and various forms, modifications and combinations of these processes such as the alkaline sulphite process for example. While any chemical pulp lignocellulosic fibre may be used, we have found it advantageous to use such pulp with a relatively low Kappa Number, preferably of not more than 40, and more preferably 30 or less.

In one form of the invention the chemical pulp lignocellulosic fibre is kraft or soda pulp with a Kappa Number

of not more than 35. While bleached chemical pulp lignocellulosic fibre may be used we have found this to be by no means essential, and unbleached kraft fibre is a useful cost-effective lignocellulosic fibre for use in the present invention, especially when included within the range 4% to 12% by mass of lignocellulosic fibre on a dry solids basis, although greater amounts in particular may be used in the manufacture of low density products suited to interior uses such as ceiling tiles and wall linings.

Products made in accordance with the present invention are particularly useful for exterior uses such as wall and deck cladding panels, and for roof applications such as slates, tiles, and corrugated sheets, and for these uses a range of between 6% and 8% by mass of lignocellulosic fibre is preferred, although amounts outside this range may be used for special purposes.

In the present invention, an essential component of the mixture from which the product is to be formed is selected siliceous substance (as defined herein). Selected siliceous substance has been found to have several important advantages and functions during the mixing, forming and curing steps of the methods of manufacture and compositions described and claimed herein.

We have found that inclusion of at least one selected siliceous substance having a bulk density of not more than 1200 kg per cubic metre substantially modifies the rheology of the mixture to the extent where it becomes possible to evenly disperse the chemical pulp lignocellulosic fibre without the need for a liquid phase medium in the mixture.

The mixture can be prepared in a substantially dry state with not more than 30% water by mass based upon the to all dry solids content of said mixture compared with the prior art where approximately 94% or more of water on this basis is common prior to the de-watering step. Due to the presence of at least one selected siliceous substance the mixture can be prepared in a substantially dry state, and the need for de-watering is thus avoided, providing considerable commercial advantages. The prior art limitations relating to drainage rate of the mixture are eliminated and the mixture can be formed to the required thickness in a single pass without the need to build up multiple layers, and there is no aqueous phase to contaminate with wood extractives. The manufacturing line becomes more compact, rejects are reduced, and there is no waste water for disposal.

Another advantage or function of selected siliceous substance is that it is reactive with the hydraulic cement in the mixture and assists materially in development of the set cement matrix in the fibre reinforced cement products of this invention, especially when the selected siliceous substance is calcined to at least 450°C prior to use.

The calcining or heat treating step has been found to induce or promote pozzolanicity in the mixture as well as usually decreasing the bulk density of the selected siliceous substance to advantage. We have found that this pozzolanicity offers significant advantages compared with prior art mixtures of cement and ground silica sand since these must be autoclaved in most cases to develop adequate physical properties and durability.

While the mixtures of the present invention may be autoclaved if desired, we have found that this is not usually necessary, this enabling a costly processing step commonly used in the prior art to be avoided.

In the methods of the present invention the mixture is substantially dry formed, and contains not more than 30% by weight of water. The selected siliceous substance has been found to contribute significantly to the dry forming step by promoting good flow in the mixture during formation and subsequent clamping of the formed matt prior to curing, this assisting in obtaining an even density profile in the finished product.

We have found that the mixture described herein may be formed using many conventional formers such as air formers, and those commonly used in the manufacture of particleboard and dry formed fireboard for example. Any suitable dry or semi-dry former may be used however.

After forming, the matt is compressed to stops or to a substantially pre-determined density and clamped for sufficient time to allow setting reactions to advance sufficiently to produce a handleable product. After clamping, the product which may still be frangible is allowed to post cure or condition in a suitable environment such as a humid or steam environment for example to further advance the setting reactions prior to trimming and/or finishing as required.

The matt may be clamped between cauls to allow initial setting reactions to advance sufficiently to produce a handleable product, or may be pressed directly in a suitable press which may be heated to accelerate the hydraulic cement setting reactions. In a preferred form of the invention a heated press is used to accelerate the hydraulic cement setting reactions. In a preferred form of the invention a heated press is used to compress the matt to a substantially pre-determined thickness and/or density to allow setting reactions to advance. The present plattens may be perforated to facilitate injection of saturated steam and/or chemicals to accelerate the hydraulic cement setting reactions.

The method of manufacturing fibre reinforced cement composites in accordance with the present invention wherein a mixture is prepared and formed into a matt and subsequently clamped or pressed without the need for de-watering a slurry has been found to have many advantages compared with prior art methods. Because there is no aqueous phase involved there is an opportunity to introduce water soluble additives at any stage of the process. In the prior art, Hatschek process for example, such additives could only be contained in the aqueous phase of the system.

In one form of the present invention hydraulic cement set modifiers may be added during the process. The set modifiers may be added during mixing of the components, during formation of the matter, to the matt itself prior to clamping or pressing, during clamping or pressing through perforated cauls or press plattens, or after clamping or pressing, such as prior to block stacking or by dipping the partially cured product in a suitable bath. For example, set modifiers may be added during the process to increase the setting rate of the hydraulic

cement, and the rate may be further increased by application of heat and maintenance of humidity.

Suitable set modifiers such as the metal chlorides  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{FeCl}_2$  and  $\text{AlCl}_3$ , alkali metal salt of carbonic acid, alkali metal silicate, alkali metal formate, a metal sulphate or a metal nitrate, a carboxylate, and mixtures of these compounds may be added during the process to increase the setting rate of the hydraulic cement.

In one form of the invention a suitable set modifier or mixture may be included in the matt prior to hot pressing for sufficient time to produce a rigid product when released from the hot press. The preferred hot pressing temperature is within the range  $50^\circ\text{C}$  to  $95^\circ\text{C}$  and the preferred pressing time is within the range 5 to 20 minutes.

The rigid product is preferably hot block stacked after release from the press and allowed to post cure in a stream or high humidity environment for between 2 and 24 hours prior to re-conditioning to ambient conditions. Longer post cure times may also be used if necessary or desired, and the pressing times may be increased to advantage as the product thickness increases.

The mixtures used for manufacturing fibre reinforced cement composites in accordance with the present invention may contain up to 66% of selected siliceous substance by weight on a dry solids basis, including mixtures of such substance. We have found that various amorphous forms of silica such as for example pyrogenic silica, silica fume, silica sol, silica gel, precipitated silica or a biogenic silica are particularly reactive with alkali metal hydroxide during hydration of hydraulic cement, and can be included to advantage in small amounts up to 10% in the mixtures for the purpose of accelerating the setting reactions.

In one form of the invention for example the selected siliceous substance may consist of up to 66% of the mixture by weight on a dry solids basis with up to 10% being selected from pyrogenic silica, silica fume, silica sol, silica gel, precipitated silica or a biogenic silica, with the remainder to 66% being selected from perlite, shirazu, pumice, volcanic tuff, diatomite, pozzolan, fly ash floaters, cenospheres and mixtures thereof.

The essential fibre reinforcement used in the present invention is chemical pulp lignocellulosic fibre such as soda or kraft pulp for example, which may be unbleached.

A preferred fibre is unbleached kraft pulp of softwood origin, but we do not exclude hardwood fibres which may also be used.

The chemical pulp lignocellulosic fibre may be included in the mixture in amounts of between 4% and 20% by weight on a dry solids basis, with a preferred range of between 5% and 10% by weight to suit the majority of purposes.

In addition to the essential chemical pulp lignocellulosic fibre reinforcement, any other suitable additional fibre may also be included, such as various polymer fibres, acrylic, polyester or polypropylene for example, and steel or carbon fibres for example.

Mixtures used for manufacturing fibre reinforced cement composites in accordance with the present invention may, in addition to the essential components described herein, also contain various fillers and additives such as clays, ground silica sand, non-metallic minerals, pigments, plasticisers, water reducing or retaining admixtures, waterproofing admixtures, shrink compensators, set accelerators, set retarders, gas forming agents, air entraining agents and polymer additives such as polymers and co-polymers of acrylamide and/or methacrylamide, and/or polyester and/or polyvinyl acetate and/or polystyrene for example, and methyl cellulose.

Due to the presence of selected siliceous substance, having a bulk density of not more than 1200 kg per cubic metre the mixtures used for manufacturing fibre reinforced cement composites in accordance with the present invention may be simply prepared in any suitable mixer such as a conventional blender or drum mixer for example, and the mixture may be prepared in several stages if desired, the selected siliceous substance and chemical pulp lignocellulosic fibre being mixed together, with or without water, and the hydraulic cement being mixed in at a later stage for example.

In a preferred embodiment of the invention, the mixture, after inclusion of the hydraulic cement is passed through at least one mixing stage wherein it is subjected to high shear or attrition which has been found beneficial in thoroughly dispersing the mixture components to advantage. Any suitable high shear or attrition machine may be used for this mixing stage including for example various mills and/or refiners such as hammer, ball, or rod mills for example, and either single or double disc refiners for example.

To permit the preparation of highly reactive mixtures, cooling may be employed. Any of the component materials including the water may be cooled for example, as may be the mixer or mixers and/or the formers for example, to reduce or inhibit premature reactions involving the hydraulic cement, prior to clamping or pressing. When used in conjunction with hot clamping or pressing, highly reactive cooled mixtures may be prepared and formed, and then hot pressed or clamped. We have found the mixtures to be fluid and easily formed even when cooled to below  $0^\circ\text{C}$ .

The invention will now be described by way of example only wherein the selected substance is a preferred selected siliceous substance, being perlite, shirazu, pumice, volcanic tuff, diatomite or pozzolan and mixtures thereof. We have found that these selected siliceous substances give excellent results in the present invention when used with a relatively fine particle size.

Preferably all of the particles will pass a 4.75mm screen, and more preferably a 0.6mm screen. For this reason fines may be employed to advantage both technically and economically. Perlite fines for example which are otherwise unused or of limited use for other purposes may be used to advantage in the present invention.

Preferably the selected siliceous substance has a bulk density of between 64 kg per cubic metre and 840 kg

per cubic meter and more preferably between 64 kg per cubic metre and 192 kg per cubic metre, although densities up to 1200 kg per cubic metre may be used.

The selected siliceous substance is preferably calcined or heat treated to a temperature of at least 450°C prior to use, and more preferably to a temperature of between 450°C and 750°C.

The selected siliceous substance and the chemical pulp lignocellulosic fibre such as kraft pulp fibre, preferably with a Kappa number of between 20 and 40, and more preferably with a Kappa number of between 20 and 30 (which indicates a relatively low residual lignin content in the lignocellulosic fibre) may first be mixed together either completely dry or with some water, sufficient to give not more than 30% water by mass based upon the total dry solids of the complete mixture (including all dry ingredients). The hydraulic cement may be included with the mix of selected siliceous substance, or may be added at a later time in a further mixing stage, as may other components of the mixture if desired. With the hydraulic cement excluded until a later stage, the bulk of the components may be mixed together to form a non-reactive mixture which may be stored for an extended period in a bulk storage facility for example, to have hydraulic cement added in a second mixing stage soon before forming product on a suitable former or forming station.

The second mixing stage when used is preferably of a high shear type such as a disc refiner, or a plurality thereof arranged either in series or parallel with the material flow, or a special purpose built high shear or attrition type mixing machine preferably with the mixing disc or working parts of wear resistant materials such as silicon carbide, tungsten carbide, or other suitable materials. At least the mixing machinery in the second mixing stage may be cooled to remove frictional heat and any heat of hydration from the mixture to reduce premature reactions prior to the forming and clamping or pressing stages.

Components of the mixture may also be cooled, including the water used in mixing so that more rapid curing mixtures may be used, such as the addition of up to 10% aluminium chloride for example. The hydraulic cement, which may be predominantly Ordinary Portland Cement may in one form of the invention include a high alumina cement also, to increase the rate of reaction and thereby increase productivity. Other mixtures of hydraulic cement may also be used however, and chemicals such as alkali metal silicates, formates and carbonates, including mixtures thereof may also be included if desired. For example, the mixture may contain 30% and 60% of hydraulic cement in one form of the invention, with up to 20% of this cement being a high alumina cement. In a preferred mixture between 1% and 9% of the hydraulic cement is a high alumina cement.

We have found that particularly when the selected siliceous substance is calcined perlite, shirazu, pumice, volcanic tuff, diatomite, pozzolan and mixtures thereof with a bulk density of between 64 kg per cubic metre and 840 kg per cubic metre, and more preferably between 64 kg per cubic metre and 192 kg per cubic metre, the prepared mixture containing also the fibre such as kraft fibres, the hydraulic cement, and any other desired components exhibits good flow and forming properties, enabling the formation of a matt of uniform structure and density to be simply and effectively obtaining even when the mixture is cooled to below 0°C.

The matt may be formed for example onto re-cyclable-re-used cauls, or on a continuous belt for example adapted to convey the matt into the clamping station or a press. In one form of the invention, the cauls or continuous belt is fluid permeable to allow for admission of water, chemicals and/or steam to the matt prior to or during compression to density and thickness.

The matt may be compressed for example in a press with one or more daylights, and either held until sufficiently rigid to be handled or stacked for post curing and conditioning, or a stack of cauls with matts thereon may be clamped until sufficiently cured to enable separation of the cauls and further processing of the partially cured product. The cure may be completed in a steam atmosphere at atmospheric pressure or at elevated pressure in an autoclave if desired. A significant commercial advantage of the present invention however is that the cost of autoclaving can be avoided if desired for most purposes. An aspect of the cure may also include carbonation, employing contact with either carbon dioxide or an atmosphere containing carbon dioxide, or with a solution containing a soluble carbonate.

Mainly due to the good flow characteristics of the mixture during consolidation, building components such as tiles and corrugated sheet for roofing and the like may be produced using the present invention, as well as profiled and flat cladding sheets and interior ceiling panels of either flat or profiled designed, and other products.

Using the versatile process described herein we have manufactured products with a range of thickness, densities, and properties which fall well outside the capability of the prior art Hatschek process, and the products have been made simply and affectively without the need for an aqueous slurry mixing, transport and forming system.

A comparison between prior art Hatschek process product and an example of product made in accordance with this invention is shown in Table 1.



TABLE I

	<u>Example</u> <u>Present Invention</u>	<u>Prior art Hatschek</u>
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	Density (kg/m <sup>3</sup> )	1200
	Modulus of Rupture (MPa)	1450
	Modulus of Elasticity (MPa)	9.1
	Internal Bond (KPa)	2600
10		14.1
		9400
		543

15 The prior art Hatschek product was of a typical composition, containing Portland cement and ground silica as a matrix, with 7.0% softwood kraft pulp fibre. The poor inter-lamellar bonding (low internal bond) of the Hatschek material can be clearly seen.

The example product made in accordance with the present invention contained a mixture of 6% softwood kraft pulp, 25% expanded perlite (as the selected siliceous substance) 67.6% rapid hardening portland cement (as the hydraulic cement) and 1.4% Darex (Registered Trade Mark) (as a set modifier) to which 15% water by mass based upon the total dry solids contact of the mixture was added.

20 The dry solids including the softwood kraft fibre were first tumble mixed together in a tumble mixer. A drum mixer or low speed hammer mill may be used for this purpose. The result is a low density woolly or fluffed mixture which is easily transported on conveyor. After adding the water, the mixture was passed through a high shear mixing stage which in our example consisted of two passes through a standard double disk refiner. After passing the refiner, the water content of the mixture was not readily apparent as it was still very fluffy and easily conveyed, and readily discharged from bins and forming devices.

25 The apparently dry mixture was laid down in a desired thickness calculated to give an appropriate dry density in the finished panel product, and pressed at 1300 KPa pressure in a hot press for between 5 and 15 minutes at a platten temperature of between 95°C and 45°C. The panels which were still frangible when removed from the hot press were block stacked and post cured for 30 days in a high humidity environment prior to testing.

30 Unlike the Hatschek process, the process of the present invention is versatile and simple, and materials with a density range between 400 and 2000 kg per cubic metre can be produced on a single compact production line in a range of thicknesses. Textured or patterned surfaces may be generated by pressing against suitable cauls during the consolidation step.

35 If desired the chemical pulp lignocellulosic fibre may be pre-treated prior to incorporation in the mixture for the purpose of improving conditions at the fibre cement interface, particularly the interface bond and inhibiting the deleterious effects of lignin and various extractives thereat.

40 Prior art treatments with various aqueous solutions containing alkali metal silicates or phosphates, chromate, permanganate chloride or sulphate, aluminium chloride or sulphate, or borax for example.

The invention provides a useful process and products in the field of fibre reinforced cement composites which avoid or minimise many of the problems found at present in the prior art.

45 The invention has been described by way of example only. Modifications and variations will be apparent to those skilled in the art and may be made thereto, without departing from the scope of the invention, as defined in the appended claims.

## 50 Claims

1. A method of forming fibre reinforced cement composites, including the steps of:

55 a) preparing a mixture including dry solids and not more than 30% water by mass based upon the total mass of dry solids, said dry solids including at least one hydraulic cement, chemical pulp lignocellulosic fibre and at least one selected siliceous substance;

b) forming and pressing said mixture to predetermined density and/or dimension; and

c) maintaining conditions of high humidity for sufficient time to advance setting reactions in said mixture to product a fibre reinforced product.

60 2. A method as claimed in claim 1, wherein preparation of said mixture includes high shear and/or attrition mixing.

3. A method as claimed in claim 1 or claim 2, wherein said one or more selected siliceous substances are calcined prior to use by heat treating to a temperature of at least 450°C.

4. A method as claimed in any one of the preceding claims, wherein said forming and pressing step includes hot pressing.

65 A method as claimed in claim 4, wherein said hot pressing is conducted at a temperature within the range 50

to 95°C, for a pressing time within the range 5 to 20 minutes.

6. A fibre reinforced cement product, formed by a method as claimed in any one of the preceding claims.

7. A product as claimed in claim 6, wherein said dry solids include, by mass, 30% to 60% of said at least one hydraulic cement, 4% to 20% of said chemical pulp cellulosic fibre and 6% to 50% of said at least one selected siliceous substance.

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8. A product as claimed in any one of the preceding claims 6 or 7, wherein said mixture includes said at least one selected siliceous substance, and at least one further more pozzolanic siliceous substance.

9. A product as claimed in any one of the preceding claims, wherein said chemical pulp lignocellulosic fibre has a kappa number of between 20 and 40.

10. As claimed in any one of the preceding claims 6-9, wherein said dry solids include 4% to 12% of chemical pulp lignocellulosic fibre.

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11. A product as claimed in claim 6, including up to 66% of said one or more selected siliceous substances by weight on a dry solids basis.

12. A product as claimed in any one of the preceding claims 6-11, wherein said one or more selected siliceous substances are of a particle size such that said particles will pass a 4.75mm screen.

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13. A product as claimed in any one of the preceding claims 6-12, wherein said selected siliceous substance has a bulk density between 64 and 192 kg per cubic metre.

14. A method as claimed in claim 1, substantially as hereindescribed.

15. A fibre reinforced cement product as claimed in claim 6, substantially as hereindescribed.

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 88307945.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	DD - A1 - 240 192 (TECHNISCHE UNIVERSITAT DRESDEN) * Totality * --	1	C 04 B 18/26 C 04 B 16/02 C 04 B 28/02
X	GB - A - 2 170 141 (TAC CONSTRUCTION MATERIALS LIMITED) * Totality * ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 04 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 07-12-1988	Examiner BECK
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			